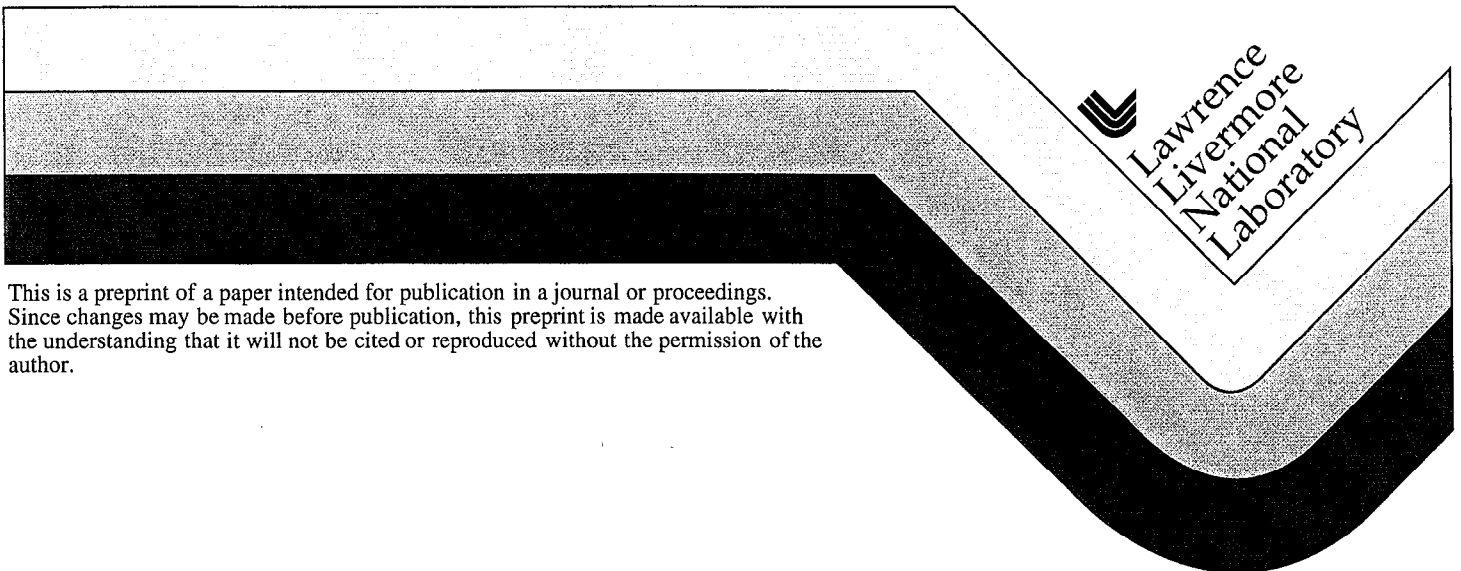


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Integrated Quantum-mechanical Approach to Stability, Chemical Order and Phase Evolution in Complex Alloys

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Abstract

We first briefly review and illustrate the application of a state-of-the-art approach to the study of phase stability properties of substitutional alloys based on periodic lattices with the prediction of the phase diagram of Ta-W. Then, we schematically present a real-space approach based on electronic structure calculations for studying stability, chemical order and phase evolution in the case of multi-component alloys which exhibit both chemical order and topological disorder. Potential applications, and preliminary results will be discussed.

Introduction

During the last fifteen years or so, first-principles based approaches to the study of stability and order, and the prediction of phase diagrams have been proposed and applied to various substitutional alloys with a fair degree of success [1]. Most applications dealt with alloys based on simple crystalline structures. It remains that a new step in the formal development has to be reached to make possible the investigation of the interplay between topological disorder and chemical short-range order (SRO), and their impact on properties and design, in alloys with reduced symmetry, such as in the presence of defects (interface, surface, grain boundary, dislocation, etc.), or in the absence of any symmetry, as in the case of amorphous materials. Indeed a broad class of problems, including in particular the study of the liquid state of an alloy with an electronic structure-based approach is still challenging this field of research. We present in this paper the basic elements required to tackle these studies starting with a brief review of what has been done so far to describe periodic alloys and their stability properties.

Methodologies and Results

When dealing with the atomistic description of chemical order in alloys, one has to combine electronic structure calculations with a statistical treatment to estimate the free energy as a function of temperature, concentration, and eventually pressure. By analogy with the problem of magnetism in alloys, it is tempting to map the quantum mechanical description of the energetics of an alloy onto an Ising Hamiltonian. This mapping has been originally achieved within the so-called generalized perturbation method (GPM) [1], which treats the fluctuations of local concentration in a reference medium which is as close as possible to any chemical configuration of the alloy. Such suitable medium is given by the chemically disordered state, as described within the coherent potential approximation (CPA) [1,2]. Subsequently, the method has been generalized to account for chemical correlations inside finite clusters embedded in the CPA-reference medium with the embedded cluster method (ECM) [3]. In both methods, only the configuration-dependent contribution to the total energy is expressed by an expansion in terms of effective pair and multi-site interactions, and since the reference medium is concentration-dependent, so are these interactions. Within the ECM, the configurational (or ordering) energy for a binary alloy is given by

$$\Delta E_{\text{ord}}(\{p_n\}) = \sum_n h_n \delta c_n + \sum_{n,m \neq n} V_{nm} \delta c_n \delta c_m + \dots \quad (1)$$

where δc_n refers to the fluctuation of concentration on site n , $\delta c_n = p_n - c$, where c is the concentration in B-species, and p_n is an occupation number associated with site n , equal to 1 or 0

depending on whether or not site n is occupied by a B-species. The h_n are the effective on-site energies which act as chemical potentials. Because of the properties of the reference medium, an expansion up to two-body interactions is usually enough to provide the required accuracy. The effective pair interaction (EPI), V_{nm} , between sites n and m is given by the expression: $V_{nm} = V_{nm}^{AA} + V_{nm}^{BB} - 2V_{nm}^{AB}$, which indicates that if the EPI (for these particular sites) is positive, it favors the formation of an AB-pair (tendency towards ordering), otherwise it favors the formation of an AA or a BB pair (tendency towards clustering). As expected on simple physical grounds, the EPIs are concentration-dependent, and lead to a wide variety of scenarios regarding alloy behavior with composition, as observed experimentally.

Once these interactions are known, the ground-state properties of the alloy at zero-temperature can be predicted. And finally, combined with a statistical model such as the cluster variation method (CVM) or with Monte Carlo (MC) simulations, the configurational part of the free energy can be computed, and hence, phase stability properties can be summarized as functions of temperature and concentration [1]. As an illustration, we now briefly present the results for bcc-based Ta-W alloys. The electronic structure calculations have been performed with the tight-binding linear muffin-tin orbital (TB-LMTO) methodology within the CPA and combined with the GPM to describe the energetics of this alloy. In Figures 1a and b, we present the formation (or mixing) energy, ΔE_{mix} , and the first and second neighbor EPIs, V_1 , and V_2 , as functions of alloy composition. Both results indicate a tendency toward phase formation, a departure from the known phase diagram which points toward solid solution behavior with no formation of intermediate phases. The ground-state analysis based on the predicted EPIs shows that B2 (of CsCl-type) and DO₃ at TaW and Ta₃W are favored at zero temperature. The further application of the CVM in the irregular tetrahedron formed by three first neighbor and one second neighbor pairs leads to the phase diagram displayed in Fig. 1c. Although very little work has been done experimentally on this phase diagram, there is indication from experiment [4] that the Ta-W should exhibit a tendency towards order, based on the negative departure from linearity of the variation of the lattice constant with alloy composition, a result (not shown here) which is well reproduced with our calculations.

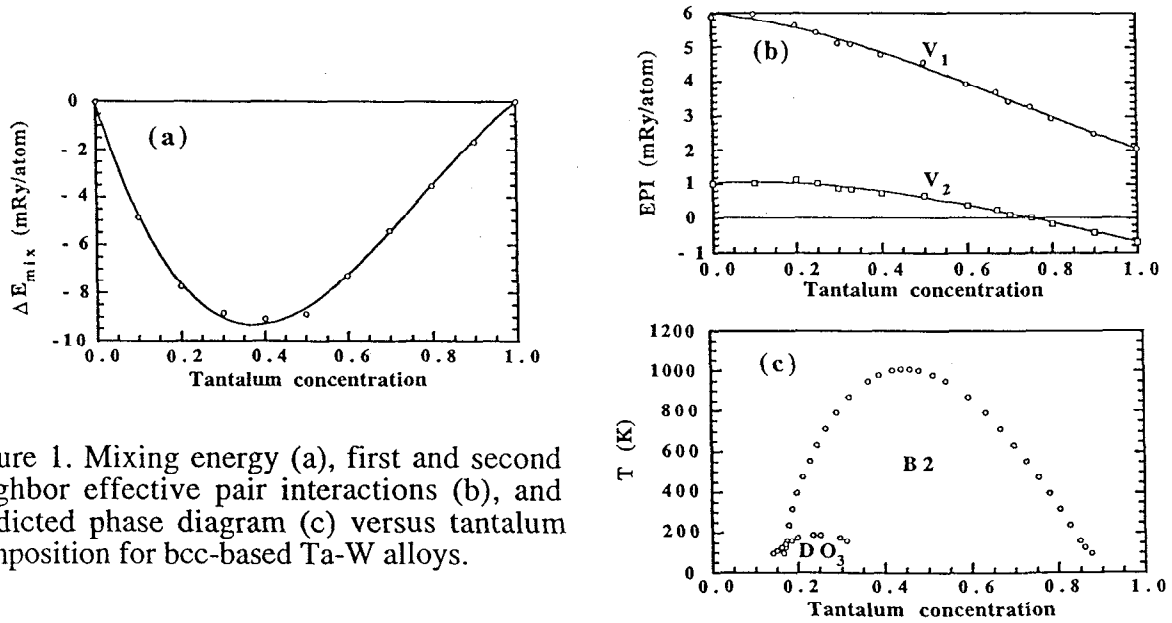


Figure 1. Mixing energy (a), first and second neighbor effective pair interactions (b), and predicted phase diagram (c) versus tantalum composition for bcc-based Ta-W alloys.

To extend such methodology to alloys based on complex lattices in the presence of extended defects, as well as to topologically (structurally) disordered materials, one has to devise efficient algorithms, preferably in real-space, to solve the CPA equations in the case of an inhomogeneous system (multi-site case), and second, obtain the EPIs which will build up the configurational part of the total energy. This was accomplished recently with the use of an extended-recursion scheme for the solution of the CPA equations, and the orbital peeling technique for the evaluation of the EPIs within the ECM [5]. The energetic information can then be used with canonical MC simulations to predict the chemical configuration of a given alloy.

The lattice on which the alloy is based is then relaxed with TB-MD simulations. This integrated scheme is represented in Figure 2.

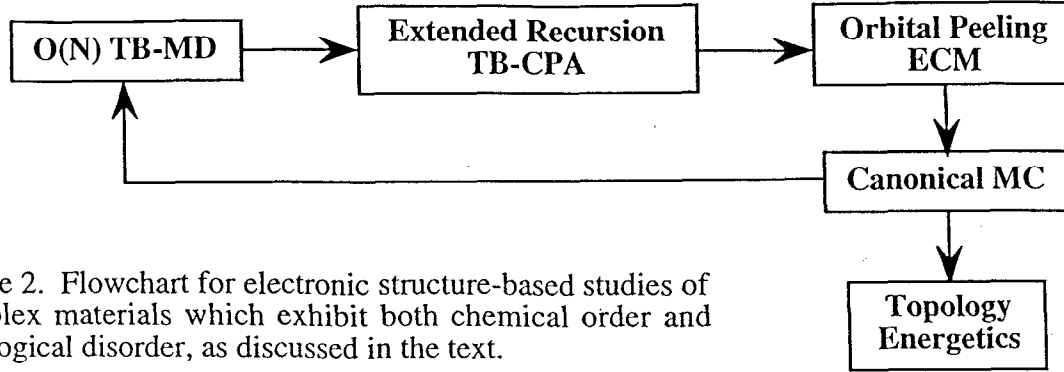


Figure 2. Flowchart for electronic structure-based studies of complex materials which exhibit both chemical order and topological disorder, as discussed in the text.

The different time scales which are usually involved are now taken care of within a consistent electronic structure framework (here, TB). More specifically, MD solves the short time scale issues of vibrations and relaxations whereas MC solves the long time scale of atomic diffusion and precipitation, and therefore both chemical and topological disorders are treated on the same footing. It should be added that in the TB framework, two types of disorder are usually encountered, namely the so-called diagonal and off-diagonal disorders, which account for the difference in on-site energies and in electronic bandwidth of the species constituting the alloy, respectively. Recently, it was shown that the extension to the case of off-diagonal disorder within the Shiba approximation [6] could be achieved with minor modifications to the extended-recursion scheme. Hence, this methodology leads to an accurate description of the electronic structure properties of alloys in the multi-orbital, multi-site, and multi-species cases. Since the formalism does not assume any periodicity (description entirely in real space), and the recursion procedure scales with the number of sites, the resulting codes can be advantageously implemented on massively parallel machines with an almost ideal load balance.

To demonstrate the validity and the accuracy of the real-space methodology, a number of numerical tests were carried out for various multi-component alloys, in the multi-orbital case (spd-atomic orbital basis), with TB parameters determined within the TB-LMTO approach [7]. Figure 3 shows that the CPA-densities of states (DOSs) for a bcc-based ZrRh random alloy, in which case both diagonal and off-diagonal disorders are treated, obtained with the real-space extended recursion and the standard k-space approaches [6] compare favorably.

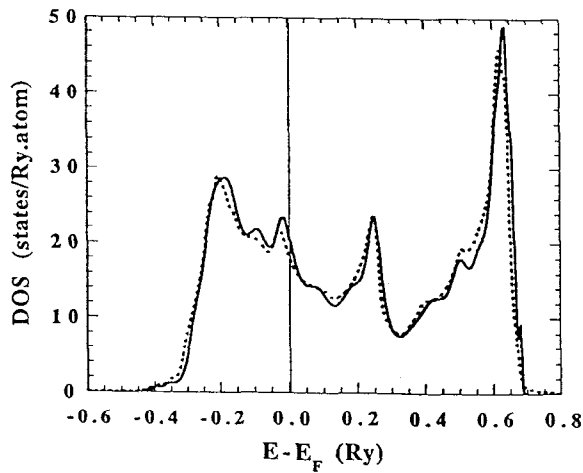


Figure 3. Density of states of a bcc-based ZrRh disordered alloy as a function of energy (the Fermi energy is taken as zero of energy), as obtained from real-space (solid line) and k-space (dotted line) calculations.

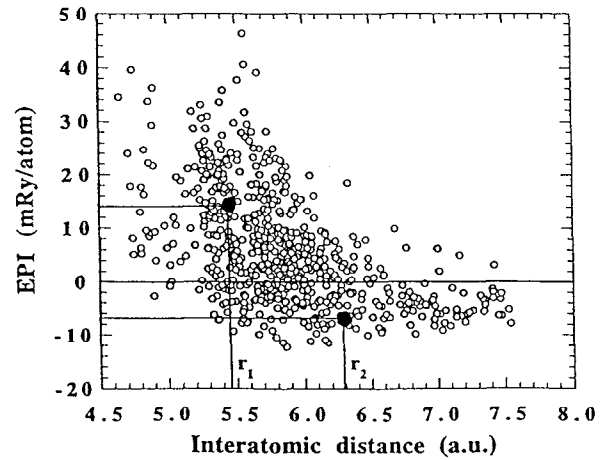


Figure 4. Effective pair interactions for an amorphous configuration of Zr_2Ni as functions of distance (the two solid circles indicates the values of the first and second EPIs for the corresponding bcc-based alloy).

Preliminary application of the integrated approach schematically described in Fig. 2 to the case of amorphous Zr-Ni alloys clearly shows that the EPIs, depend not only on alloy composition, as in the periodic case, but also on the local distribution of atoms. This is illustrated in Fig. 4 in the case of an amorphous configuration of Zr_2Ni [8]. Consistent with the clear tendency towards order predicted in the corresponding case of the crystalline phase of Zr_2Ni with a bcc structure (see Fig. 4, with the first two EPIs being equal to about +14.1 and -6.3 mRy/atom), the mean value of the EPIs obtained in the amorphous case is positive and decreases with distance. However, it is worth noting that, for a given neighbor distance, the EPIs can be either positive or negative. This noticeable scattering can be attributed not only to the renormalized character of the interactions which includes the overall scattering of the electrons throughout the alloy as accounted for within the ECM, but also to the influence of the local topology around a given pair of atoms. This property, which is totally neglected in approaches which use phenomenological potentials, indicates that a fair amount of frustration is built into the alloy, and order-disorder phenomena in these instances remind us of the analogy with spin glasses [9] for which more detailed studies have been performed than in the case of structural glasses. This opens up the possibility of applying concepts and techniques used in another field (such as the replica and the "Thouless-Anderson-Palmer" approaches) to analyze the glass transition and the nature of the glassy state with a methodology which solely relies on input from electronic structure theory.

Conclusions

The methodology presented here is well suited for addressing stability and chemical order issues in multi-component alloys with reduced or no symmetry. It is applicable to the study of a wide class of problems, among others: (i) the description of the liquid state, and the inclusion of the vibrational energy and entropy, and the energy due to the relaxation of the lattice in the calculation of the total Gibbs energy for a more complete prediction of phase diagrams; (ii) reconstruction, relaxation, ordering and concentration profile for alloys in the presence of surfaces; (iii) diffusion at interfaces in bulk and multi-layered materials; (iv) and finally, the more general phenomenon of nucleation and growth in alloys.

Acknowledgments

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